The ground state of $Sr_3Ru_2O_7$ revisited; Fermi liquid close to a ferromagnetic instability

Shin-Ichi Ikeda[1,2], Yoshiteru Maeno[2,3], Satoru Nakatsuji[2], Masashi Kosaka[4], and Yoshiya Uwatoko[4]
[1]*Electrotechnical Laboratory, Tsukuba, Ibaraki 305-8568 , Japan*
[2]*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*
[3]*CREST, Japan Science and Technology Corporation, Kawaguchi, Saitama 332-0012, Japan*
[4]*Department of Physics, Saitama University, Saitama 338-8570, Japan*

(Received)

We show that single-crystalline $Sr_3Ru_2O_7$ grown by a floating-zone technique is an isotropic paramagnet and a quasi-two dimensional metal as spin-triplet superconducting Sr_2RuO_4 is. The ground state is a Fermi liquid with very low residual resistivity ($\approx$3 $\mu\Omega$cm for in-plane currents) and a nearly ferromagnetic metal with the largest Wilson ratio $R_W \geq 10$ among paramagnets so far. This contrasts with the ferromagnetic order at T_C=104 K reported on single crystals grown by a flux method [Cao *et al.*, Phys. Rev. B **55**, R672 (1997)]. However, we have found a dramatic changeover from paramagnetism to ferromagnetism under applied pressure. This suggests the existence of a substantial ferromagnetic instability in the Fermi liquid state.

PACS number(s): PACS numbers: 75.40.-s, 71.27.+a, 75.30.Kz

The discovery of superconductivity in the single-layered perovskite Sr_2RuO_4 [1] has motivated the search for new superconductors and anomalous metallic materials in Ruddlesden-Popper (R-P) type ruthenates $(Sr,Ca)_{n+1}Ru_nO_{3n+1}$. The recent determination of the spin-triplet pairing in its superconducting state suggests that ferromagnetic (FM) correlations are quite important in Sr_2RuO_4 ,[2] and the existence of enhanced spin fluctuations has been suggested by nuclear magnetic resonance (NMR) .[3,4] On the other hand, the recent report has shown that enhanced magnetic excitations around $\mathbf{q}$=0 is not detected but sizeable excitations have been seen around finite $\mathbf{q}$ in Sr_2RuO_4 by inelastic neutron scattering.[5] This has stimulated debate on the mechanism of the spin-triplet superconductivity, which had been naively believed to have a close relation to FM ($\mathbf{q}$=0) spin excitations. Hence, it is desirable to investigate its related compounds as described below.

The simple perovskite (three dimensional) metallic $SrRuO_3$ ($n = \infty$) has been well known to order ferromagnetically below 160 K with a magnetic moment $M = 0.8 \sim 1.0\mu_B$/Ru .[6,7] FM perovskite oxides are relatively rare except for metallic manganites. For pure thin film $SrRuO_3$, analyses of quantum oscillations in the resistivity have given good evidence for the Fermi liquid behavior .[8]

The double layered perovskite $Sr_3Ru_2O_7$ (n=2) is regarded as having an intermediate dimensionality between the systems with $n = 1$ and $n = \infty$.[9] Investigations on polycrystalline $Sr_3Ru_2O_7$ showed a magnetic-susceptibility maximum around 15 K with Curie-Weiss-like behavior above 100 K and a metallic temperature dependence of the electrical resistivity .[10,11]

In the study presented here, we have for the first time succeeded in growing single crystals of $Sr_3Ru_2O_7$ by a floating-zone (FZ) method. Those single crystals (FZ crystals) do not contain any impurity phases (e.g. $SrRuO_3$) which was observed in polycrystals .[11] We report herein that the FZ crystal of $Sr_3Ru_2O_7$ is a nearly FM paramagnet (enhanced paramagnet) and a quasi-two dimensional metal with a strongly-correlated Fermi liquid state. In addition, we have performed magnetization measurements under hydrostatic pressures up to 1.1 GPa in order to confirm whether the FM instability is susceptible to pressure. The results suggest that there is a changeover from paramagnetism to ferromagnetism, indicating a strong FM instability. Essential features of magnetism for FZ crystals as well as polycrystals are inconsistent with the appearance of a FM ordering (T_c = 104K) at ambient pressure for single crystals grown by a flux method [12] using $SrCl_2$ flux and Pt crucibles. We will argue that FZ crystals reflect the intrinsic behavior of $Sr_3Ru_2O_7$.

Details of the FZ crystal growth are explained elsewhere .[13] The crystal structure of the samples at room temperature was characterized by powder x-ray diffraction. Electrical resistivity $\rho(T)$ was measured by a standard four terminal dc-technique from 4.2 K to 300 K and by an ac method from 0.3K to 5K. Specific heat $C_P(T)$ was measured by a relaxation method from 1.8 K to 35 K (Quantum Design, PPMS). The temperature dependence of magnetic susceptibility $\chi(T) \equiv M/H$ from 2 K to 320 K was measured using a commercial SQUID magnetometer (Quantum Design, MPMS-5S). For magnetization measurements of FZ crystals at ambient pressure, we performed sample rotation around the horizontal axis, normal to the scan direction, using the rotator in MPMS-5S. We could align the crystal axes exactly parallel to a

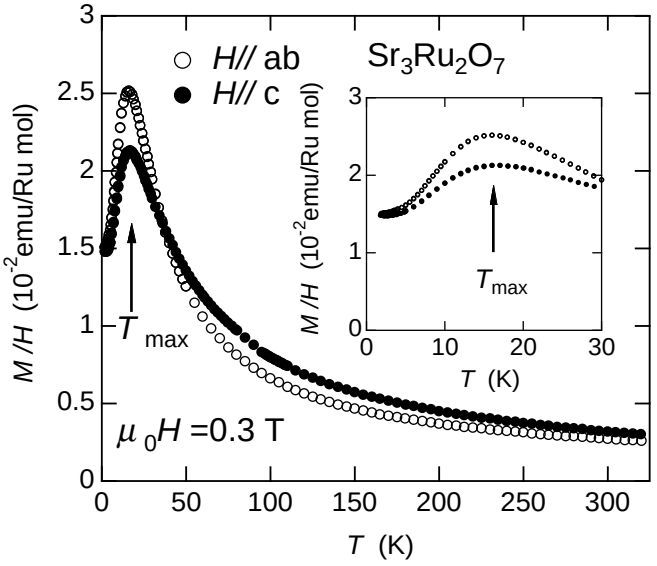

FIG. 1. Magnetic susceptibility of FZ crystals of $Sr_3Ru_2O_7$ under 0.3 T field above 2 K. The inset shows the low temperature magnetic susceptibility against temperature T.

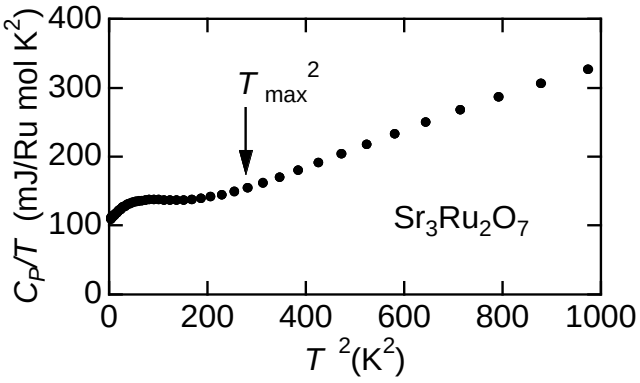

FIG. 2. Specific heat devided by temperature C_P/T of FZ crystals of $Sr_3Ru_2O_7$ above 2 K. C_P/T is plotted against T^2.

field direction within 0.2 degree using this technique. For high pressures, we measured magnetization using a long-type hydrostatic pressure micro-cell [14] with the SQUID magnetometer. Loaded pressures around 3 K were determined from the shift of superconducting transition temperature of Sn in the micro-cell in a 5 mT field .

The R-P type structure of n=2 for FZ crystals of $Sr_3Ru_2O_7$ was confirmed by the powder x-ray diffraction patterns with crushed crystals, which indicated no impurity peaks. Recently, the crystal structure of polycrystalline $Sr_3Ru_2O_7$ has been refined by neutron powder diffraction .[15,16] Although they have concluded that symmetry of the structure is orthorhombic owing to the rotation of the RuO_6 octahedron about the c-axis by about 7 degrees, we deduced lattice parameters at room temperature by assuming tetragonal $I4/mmm$ symmetry as a = 3.8872(4)Å, and c = 20.732(3)Å. These values are in good agreement with those of polycrystals obtained by neutron diffraction [15,16] and x-ray diffraction .[11]

The temperature dependence of magnetic susceptibility $\chi(T) = M/H$ in a field of 0.3 T is shown in Fig. 1. No hysteresis is observed between zero-field cooling (ZFC) and field cooling (FC) sequences, so we conclude that there is no ferromagnetic ordering. Little magnetic anisotropy is observed in contrast to large anisotropy ($\approx 10^2$) of flux-grown crystals .[12] The nearly isotropic susceptibility of $Sr_3Ru_2O_7$ is qualitatively similar to that of the enhanced Pauli-paramagnetic susceptibility in Sr_2RuO_4 .[17] For an applied field of 0.3 T, there is no in-plane anisotropy of the susceptibility for the whole temperature range (2 K $\leq T \leq$ 300K), within the precision of our equipment (1%).

The susceptibility for both $H//$ab and $H//$c exhibits Curie-Weiss behavior above 200 K. We have fitted the observed $\chi(T)$ from 200 K to 320 K with $\chi(T) = \chi_0 + \chi_{\rm CW}(T)$, where χ_0 is the temperature independent term and $\chi_{\rm CW}(T) = C/(T - \Theta_{\rm W})$ is the Curie-Weiss term. The effective Bohr magneton numbers $p_{\rm eff}$ deduced from C are $p_{\rm eff}$ = 2.52 (2.99) and $\Theta_{\rm W}$ =− 39 K (− 45 K) for $H//ab(H//c)$. The negative values of $\Theta_{\rm W}$ normally indicate antiferromagnetic (AFM) correlations in the case of localized-spin systems. However, we cannot conclude that AFM correlations play an important role solely by the negative $\Theta_{\rm W}$ in an metallic system like $Sr_3Ru_2O_7$.[18]

Around $T_{\rm max}$ =16 K, $\chi(T)$ shows a maximum for both $H//$ab and $H//$c. The maximum has been also observed in the polycrystals. The results of temperature dependence of specific heat, NMR [19] and elastic neutron scattering [15,16] for polycrystals indicate that there is no evidence for any long range order with definite moments. The FZ crystal shows nearly isotropic $\chi(T)$ for all crystal axes below $T_{\rm max}$. Hence, the maximum cannot be accredited to the long range AFM order. Therefore, we conclude $Sr_3Ru_2O_7$ to be a *paramagnet*. Concerning $\chi(T)$ under higher fields, $T_{\rm max}$ is suppressed down to temperatures below 5 K above 6 T .[20] Such a maximum in $\chi(T)$ and a field dependent $T_{\rm max}$ are often observed in a nearly ferromagnetic (enhanced paramagnetic) metal like $TiBe_2$ [21] or Pd .[22] In addition, a similar behavior in $\chi(T)$ has been observed in $(Ca,Sr)_2RuO_4$ [23] and MnSi ,[24] which are recognized as examples of a critical behavior by spin fluctuations. Similar critical behavior, originating especially from FM spin fluctuations, is also expected in $Sr_3Ru_2O_7$. Nevertheless, we cannot rule out the possibility of AFM correlations as observed in Sr_2RuO_4, caused by the nesting of its Fermi surfaces with the vector $\mathbf{Q} = (\pm 0.6\pi/a, \pm 0.6\pi/a, 0)$.[5]

As shown in Fig.2, the specific heat coefficient of the FZ crystal of $Sr_3Ru_2O_7$ is γ = 110 mJ/(K^2 Ru mol) somewhat larger compared to other R-P type ruthenates {γ =80 mJ/(K^2 Ru mol) for $CaRuO_3$, 30 mJ/(K^2 Ru mol) for $SrRuO_3$ [7] and 38 mJ/(K^2 Ru mol) for Sr_2RuO_4 [17,25]}. This suggests that $Sr_3Ru_2O_7$ is a strongly-correlated metallic oxide. For polycrystalline $Sr_3Ru_2O_7$, we obtained the value γ = 63 mJ/(K^2 Ru mol) using an adiabatic method .[11]

The temperature dependence of the electrical resistivity $\rho(T)$ is shown in Fig. 3 above 0.3 K. Both $\rho_{\rm ab}(T)$ and

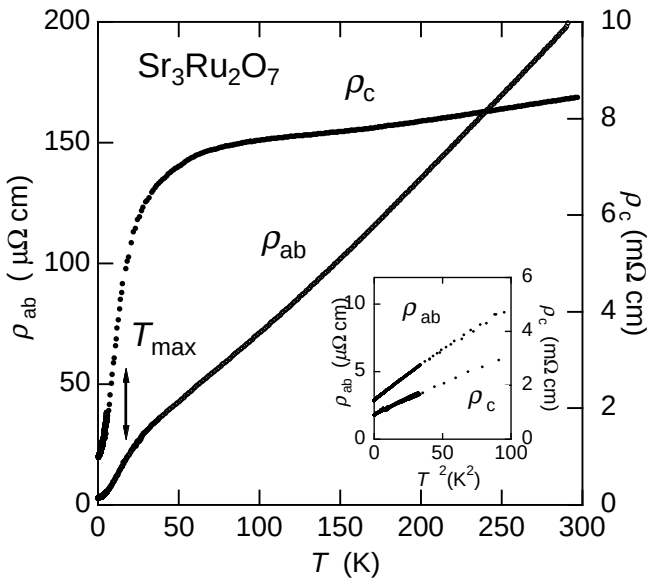

FIG. 3. Electrical resistivity of FZ crystals of $Sr_3Ru_2O_7$ above 0.3 K. Both ρ_{ab} and ρ_c are shown. The inset shows the low temperature electrical resistivity against the square of temperature T^2.

$\rho_c(T)$ are metallic ($d\rho/dT > 0$) in the whole region. The ratio of ρ_c/ρ_{ab} is about 300 at 0.3 K and 40 at 300 K. This anisotropic resistivity is consistent with the quasi-two-dimensional Fermi surface sheets obtained from the band-structure calculations .[26] With lowering temperature below 100 K, a remarkable decrease of $\rho_c(T)$ is observed around 50 K. This is probably due to the suppression of the thermal scattering with decreasing temperature between quasi-particles and phonons as observed in Sr_2RuO_4 .[17,27,28] Thus, below 50K, interlayer hopping propagations of the quasi-particle overcome the thermal scattering with phonons. This hopping picture for $\rho_c(T)$ is well consistent with the large value of $\rho_c(T)$ and nearly cylindrical Fermi surfaces. On the other hand, $\rho_{ab}(T)$ shows a change of the slope around 20 K. Such a change in $\rho_{ab}(T)$ has also been reported for Sr_2RuO_4 under hydrostatic pressure (≈ 3 GPa). That might be possibly due to the enhancement of ferromagnetic spin fluctuations .[27]

As shown in the inset of Fig. 3, the resistivity yields a quadratic temperature dependence below 6 K for both $\rho_{ab}(T)$ and $\rho_c(T)$, characteristic of a Fermi liquid as observed in Sr_2RuO_4 .[17] We fitted $\rho_{ab}(T)$ by the formula $\rho_{ab}(T)=\rho_0+AT^2$ below 6 K and obtained ρ_0=2.8 $\mu\Omega$ cm and A=0.075 $\mu\Omega$cm/K^2. Since the susceptibility is quite isotropic and temperature independent below 6 K, the ground state of $Sr_3Ru_2O_7$ is ascribable as a Fermi liquid. We now can estimate Kadowaki-Woods ratio A/γ^2. Assuming that electronic specific heat $\gamma = 110$ mJ/(K^2 Ru mol) is mainly due to the ab-plane component, we obtain $A/\gamma^2 \approx A_{ab}/\gamma^2 = 0.6 \times 10^{-5}\mu\Omega$ cm/(mJ/K^2 Ru mol)^2 close to that observed in heavy fermion compounds.

Regarding to $\chi(T)$ again, it is important to note that even at temperatures much lower than T_{max}, $\chi(T)$ remains quite large. It appears that the ground state maintains a highly enhanced value of 1.5×10^{-2} emu/Ru mol, comparable to that obtained for typical heavy fermion compounds. Considering that the observed χ is dominated by the renormalized quasi-particles, we can estimate the Wilson ratio $R_W = 7.3 \times 10^4 \times \chi$(emu/mol)/$\gamma$(mJ/(K^{2}mol)) in the ground state. If we regard the observed values at $T = 2$ K as that at $T = 0$ K, we have $R_W = 10(18)$ using γ for single crystals (polycrystals). Despite the difference in the γ value between polycrystals and single crystals, R_W is much greater than unity. This large value implies that FM correlations are strongly enhanced in this compound, especially when compared with the values of 12 for $TiBe_2$ and 6 for Pd .[29] Therefore, the ground state of $Sr_3Ru_2O_7$ is characterized by strongly-correlated Fermi liquid behavior with enhanced FM spin fluctuations, i.e. $Sr_3Ru_2O_7$ is a strongly-correlated nearly FM metal.

Concerning this FM correlations, it should be noted that, using single crystals grown by a chlorine flux method with Pt crucibles ,[30] Cao *et al.* have investigated remarkable magnetic and transport properties of R-P ruthenates [12] prior to our crystal growth. The ground state of $Sr_3Ru_2O_7$ was concluded to be an itinerant *ferromagnet* with $T_c = 104$ K and an ordered moment $M = 1.2$ μ_B/Ru. The flux-grown crystals were reported to have a residual resistivity ($\rho_0 = 3$ mΩ cm) 10^3 times greater than that of FZ crystals ($\rho_0 = 3\mu\Omega$ cm) for in-plane transport. In addition, FZ crystals reveal T-square dependent resistivities at low temperatures as already shown, which was not observed in flux-grown crystals. In general, the FZ method with great care can be impurity-free crystal growth, while the flux method tends to contaminate crystals due to impurity elements from both the flux and the crucible. This might be a main reason why the resistivity is much higher for flux-grown crystals. Thus, we suppose with assurance that the data from FZ crystals reflect the intrinsic nature of $Sr_3Ru_2O_7$ better than those from flux-grown crystals.

In order to acquire the information of the magnetic instability in the FZ crystal of $Sr_3Ru_2O_7$, we have measured magnetization under hydrostatic pressure up to 1.1 GPa. The temperature dependence of magnetization $M(T)$ is shown for several pressures under a 0.1 T field along c-axis in Fig. 4. Around 1 GPa, substantial increase is recognized below around 70 K with a clear FM component indicated by the difference between ZFC and FC sequences. Although the remanent moment at 2 K ($M \approx 0.08$ μ_B/Ru) is much smaller than that expected for S=1 of Ru^{4+}, its susceptibility is quite large (0.4 emu/Ru mol). We infer that this transition is a FM ordering of itinerant Ru^{4+} spins. In Fig. 4, we also show the field dependence of magnetization $M(H//c)$ at 2 K for $P = 0.1$ MPa and $P = 1$ GPa. Obvious ferromagnetic component appears at lower fields for $P = 1$ GPa. Even at higher fields, increase in magnetization by pressure is also present as at lower fields. This feature endorses the drastic changeover from paramagnetism to ferromagnetism induced by applied pressure. To the best of our knowledge, this is the first example of the pressure-

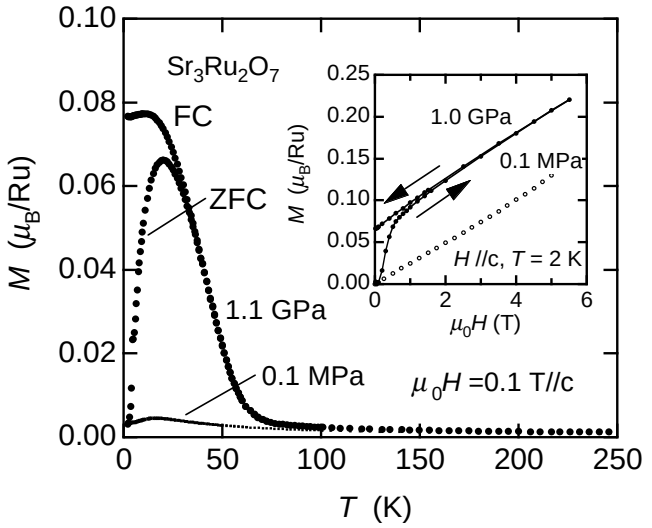

FIG. 4. Pressure dependence of magnetization $M(T)$ for $H//c$. Obvious ferromagnetic ordering appears at about 70 K under 1 GPa pressure. The inset shows the field dependence of magnetization $M(H)$ under 0.1 MPa and 1 GPa pressures.

induced changeover from Fermi liquid to ferromagnetism.

For the purpose of understanding the observed behavior, we should begin with Stoner theory. In the metallic state with correlated electrons, the ferromagnetic order is driven by the Stoner criterion $U_{\rm eff}N(E_{\rm F}) \geq 1$, where $U_{\rm eff}$ is an effective Coulomb repulsion energy. The systematics of band-width W and the density of states $N(E_{\rm F})$ in the R-P ruthenates is summarized by Maeno *et al* .[31] In this system, increasing n from 1 to ∞ causes enhancement of $N(E_{\rm F})$ as well as W. This is opposite to the single band picture, i.e. increasing $N(E_{\rm F})$ naively means decreasing W. In the case of R-P ruthenates, the anomalous variation might be due to the modifications of the degeneracy of three t_{2g} orbitals for Ru-4d electrons. According to the summary ,[31] ferromagnetic $SrRuO_3$ is characterized by the highest $N(E_{\rm F})$ and W among them, satisfying the Stoner criterion. This implies that the enlargement of $N(E_{\rm F})$ and W reflects stronger three dimensionality in the R-P ruthenates. Hence, applying pressure probably makes $Sr_3Ru_2O_7$ closer to $SrRuO_3$, leading to FM order. For further investigations, it is required that structural study, resistivity and specific heat under pressures will be performed.

In conclusion, by using the floating-zone method we have succeeded for the first time in growing single crystals of $Sr_3Ru_2O_7$ with very low residual resistivity in comparison with that of flux-grown crystals reported previously. The results of magnetization, resistivity and specific heat measurements suggest that $Sr_3Ru_2O_7$ is a strongly-correlated Fermi liquid with a nearly ferromagnetic ground state, consistent with the observation of ferromagnetic ordering below 70 K under applied pressure ($P \sim$1 GPa). As far as we know, this is the first example of the pressure-induced changeover from Fermi liquid to ferromagnetism. This ferromagnetic ordering may guarantee the existence of the ferromagnetic spin fluctuations in $Sr_3Ru_2O_7$.

Authors are very grateful to A. P. Mackenzie for his fruitful advice and critical reading of this manuscript. They thank T. Ishiguro, T. Fujita and K. Matsushige for their helpful supports. They thank S. R. Julian, G.G. Lonzarich, G. Mori, D.M. Forsythe, R.S. Perry, K. Yamada, Y. Takahashi, and M. Sigrist for their useful discussions and technical supports. They also thank N. Shirakawa for his careful reading of this manuscript.

[1] Y. Maeno *et al*., Nature(London) **372**, 532 (1994).
[2] K. Ishida *et al*., Nature(London) **396**, 658 (1998).
[3] H. Mukuda *et al*., J. Phys. Soc. Jpn. **67**, 3945 (1998).
[4] T. Imai, A. W. Hunt, K. R. Thurber, and F. C. Chou, Phys. Rev. Lett. **81**, 3006 (1998)
[5] Y. Sidis *et al*., Phys. Rev. Lett. **83** 3320 (1999).
[6] A. Kanbayasi, J. Phys. Soc. Jpn. **44**, 108 (1978).
[7] T. Kiyama *et al*., J. Phys. Soc. Jpn. **67**, 307 (1998).
[8] A. P. Mackenzie *et al*., Phys. Rev. B **58**, R13318 (1998).
[9] T. Williams, F. Lichtenberg, A. Reller, and G. Bednorz, Mat. Res. Bull. **26**, 763 (1991).
[10] R. J. Cava *et al*., J. Solid State Chem. **116**, 141 (1995).
[11] S. Ikeda, Y. Maeno and T. Fujita, Phys. Rev. B **57**, 978 (1998).
[12] G. Cao, S. McCall, and J. E. Crow, Phys. Rev. B **55**, R672 (1997).
[13] S.I. Ikeda, unpublished.
[14] Y. Uwatoko *et al*., Rev. High Pressure Sci. Technol. **7**, 1508 (1998).
[15] Q. Huang *et al*., Phys. Rev. B **58**, 8515 (1998).
[16] H. Shaked *et al*., (unpublished).
[17] Y. Maeno *et al*., J. Phys. Soc. Jpn. **66**, 1405 (1997).
[18] K. Yoshimura *et al*., Phys. Rev. Lett. **83**, 4397 (1999).
[19] H, Mukuda *et al*., (private communication).
[20] A.P. Mackenzie *et al*., (unpublished).
[21] T. Jarlborg and A. J. Freeman, Phys. Rev. B **22**, 2332 (1980).
[22] F. M. Mueller, A. J. Freeman, J. O. Dimmock, and A. M. Furdyna, Phys. Rev. B **1**, 4617 (1970).
[23] S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. **84**, 2666 (2000).
[24] C. Pfleiderer *et al*., Phys. Rev. B **55** 8330 (1997).
[25] A.P. Mackenzie *et al*., J. Phys. Soc. Jpn. **67**, 385 (1998).
[26] I. Hase and Y. Nishihara, J. Phys. Soc. Jpn. **66**, 3517 (1997).
[27] K. Yoshida *et al*., Phys. Rev. B **58**,15062 (1998).
[28] A.P. Mackenzie *et al*., Phys. Rev. Lett. **76**, 3786 (1996).
[29] S.R. Julian *et al*., Physica B **259 – 261**, 928 (1999).
[30] Hk. Muller-Buschbaum and J. Wilkens, Z. Anorg. Allg. Chem. **591**, 161 (1990).
[31] Y. Maeno, S. Nakatsuji, and S. Ikeda, Materials Science and Engineering B **63** 70 (1999).